THE DEHYDRATION OF HYDROBENZOINS

BY
STANLEY PAUL ROWLAND
B.Chem., University of Minnesota, 1938

AN ABSTRACT OF A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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CHEMISTRY IN THE GRADUATE SCHOOL OF
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Introduction

The effect of steric hindrance in stabilizing vinyl alcohols is well known[1,2] but the knowledge of the space exigencies of stable vinyl alcohols is elementary. The present investigation was undertaken with the object of preparing a series of enols exhibiting varying degrees of crowding about the two doubly-bonded carbon atoms in order to determine the structural requirement for stability in vinyl alcohols.

Discussion

The remarkable stability and simplicity of the vinyl alcohol, 1,2-dimesityl-1-propen-1-ol,[3] affords an opportunity to study the structural elements of stable enols. The molecule, 1-phenyl-2-mesityl-1-propen-1-ol, having a less hindering group on the 1-carbon atom was found to be stable for only a few hours. In air it formed a stable peroxide and in the absence of air it ketonized. Increased hindrance about the 2-carbon atom in 3-phenyl-1,2-dimesityl-1-propen-1-ol caused this enol to resist all attempts at ketonization.

β,β-Dimesitylvinyl alcohol, the most interesting and unusual of the stable vinyl alcohols, was prepared by dehydration of hydromesitoin or isohydromesitoin.[4] This stable aldehyde-enol could not be ketonized with alcoholic hydrogen chloride nor cleaved with oxygen. The vinyl alcohol reacted normally with reagents which affected the hydroxyl group; for example, it formed a benzoate. This compound was shown to be different from the enol benzoates of desoxymesitoin. Reactions in acid media which involved attack at the double bond were attended by migration of one of the mesityl groups. Thus, ozone converted the vinyl alcohol to mesitoin; chromic acid to mesitil; hydriodic acid to *s*-dimesitylethylene; and phosphorus pentachloride to dimesitylethylene dichloride. On the other hand, alkaline hydrogen peroxide and catalytic hydrogenation yield-

ed dimesityl ketone and β,β-dimesitylethanol, respectively, from the vinyl alcohol.

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VITA

The writer was born in La Crosse, Wisconsin on February 25, 1916. He received his elementary education in the public schools of Houston, Minnesota, and attended the College of St. Thomas during 1934-1936. Thereafter, he enrolled at the University of Minnesota and received the B. Chem. degree in 1938. In 1939 he began graduate study at the University of Illinois where he held teaching assistantships during 1939-1941, the Carr Fellowship during 1941-1942, and the du Pont Fellowship during 1942-1943.

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